A Phase Diagram for Morphology and Properties of Low Temperature Deposited Polycrystalline Silicon Grown by Hot-wire Chemical Vapor Deposition

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ABSTRACT

The fabrication of low temperature polycrystalline silicon with internal surface passivation and with lifetimes close to single crystalline silicon is a promising direction for thin film polycrystalline silicon photovoltaics. To achieve high lifetimes, large grains with passivated low-angle grain boundaries and intragranular defects are required. We investigate the low-temperature (300-475°C) growth of thin silicon films by hot-wire chemical vapor deposition (HWCVD) on Si (100) substrates and on large-grained polycrystalline silicon template layers formed by selective nucleation and solid phase epitaxy (SNSPE). Phase diagrams for dilute silane deposition varying substrate temperature and for pure silane varying hydrogen dilution are shown. We will discuss the relationship between the microstructure and photoconductive decay lifetimes of these undoped layers on Si (100) and SNSPE templates as well as their suitability for use in thin-film photovoltaic applications.

INTRODUCTION

HWCVD epitaxial growth on large-grained templates is one strategy for the fast low-temperature growth of large-grained films with hydrogen-passivated low-angle grain boundaries. We propose a structure by which a template with grains on the order of 10–100 μm is fabricated on ITO-coated glass or another low cost conductive substrate by a solid-phase crystallization process called SNSPE[1]. This layer serves as the n+ back surface field, and the n and p+ layers are grown epitaxially on this template by HWCVD, using phosphine and tri-methyl boron as dopants. In order to achieve this goal, investigation of the phase diagrams that lead to epitaxial growth in HWCVD are necessary. Preliminary work towards the fabrication of this cell and the necessary intermediate goals are discussed.

EXPERIMENTAL DETAILS

Dilute Silane Growth

In order to promote crystalline growth under dilute silane conditions, we used a high hydrogen partial pressure dilution ratio of 50:1, using a mixture of 4% SiH_4 in He at a partial pressure of 25 mTorr and H_2 at a partial pressure of 50 mTorr. The 0.5mm diameter tungsten wire was positioned 2.5 cm from the substrate for a growth rate of 1Å/s. The wire temperature was set to 1800°C as measured by optical pyrometry, and substrate temperatures ranged from 300°C to 475°C.

Silicon (100) substrates and large-grained polycrystalline layers formed by SNSPE were used as templates for epitaxial growth. The formation of the large-grained templates is described elsewhere[1]. The resulting polycrystalline templates have grain sizes on the order of 10 to 100 μm with low-angle grain boundaries. Before growth, both surfaces were cleaned with UV ozone for 10 minutes followed by an HF dip. Once in the chamber, they are heated at 200°C at a pressure of less than 10^{-6} Torr to desorb any residual hydrocarbons.

Pure Silane Growth

Using pure silane, the influence of dilution ratio was studied. The substrate temperature was held constant at 380 °C while graphite filaments set to 2100 °C by optical pyrometry were placed 3.5 cm from the substrate. The H_2 to SiH_4 ratio ranged from 10 to 50, total pressure also had to be adjusted for the higher H_2 flow rates and ranged from 20 to 50 mTorr. Substrates were cleaned as described above.

RESULTS

Dilute Silane Growth - Substrate temperature effects

We used TEM and RHEED to characterize the crystallinity of films grown at 50:1 hydrogen dilution and temperatures between 300-475°C in the 50 nm to 2 μm thickness regime and observed four phases of growth. A completely defect-free epitaxial phase was observable by TEM at thicknesses below 50nm; the twinned epitaxial, mixed and polycrystalline phases were observable by TEM and RHEED[2]. Twinned epitaxial silicon denotes silicon material containing twin boundaries, but no other dislocation or grain boundary defects. From this data, we derived the phase diagram in Figure 1. At 300°C, the predominant phases are epitaxial and twinned, with a transition to mixed phase or polycrystalline growth occurring somewhere between 1-2 μm of growth. As temperature increases, the epitaxial and twinned phases no longer persist and the transition to mixed phase or polycrystalline growth occurs at smaller film thicknesses. This is in direct contrast to work done by Thiesen [3] and Watahiki [4] where epitaxial thickness increased with substrate temperature. We believe that the decrease in epitaxial thickness with the increase in substrate

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temperature is due to an interplay between surface hydrogenation at low temperatures and surface oxidation at high temperatures that reduces the epitaxial thickness. This is possibly related to the higher hydrogen content in HWCVD as compared to PECVD or MBE along with oxygen contamination in the deposition chamber[5].

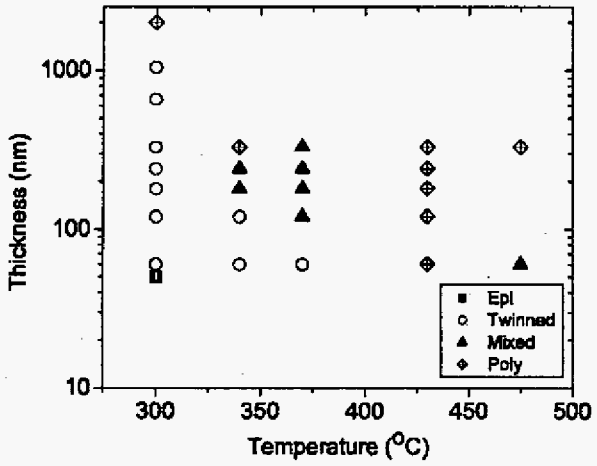

Figure 1: Phase diagram of HWCVD films grown at 50:1 hydrogen dilution with 4% SiH_4 in He.

Silicon films 300 nm thick grown on SNSPE templates under the same conditions showed epitaxial growth results consistent with local low temperature epitaxy on each of the 100 μm grains in the SNSPE templates [Fig. 2]. Epitaxial breakdown is observed in the diffraction pattern of the HWCVD film, but some of the underlying low-order diffraction spots are visible. The underlying film therefore likely has morphology similar to that of the HWCVD films on Si(100). The effect of the orientation of the underlying grain structure of the SNSPE template on the morphology of the HWCVD film is shown in Figure 2.

Cross-sectional analysis of these films reveals some areas of epitaxial growth as well as some areas of columnar growth. Before HWCVD growth, the SNSPE templates were cleaned in a solution of 3:7 HNO_3: H_2O, which has been shown by Auger spectroscopy to remove elemental Ni from the template surface[6]. The lack of epitaxy in some areas is thus more likely to have been caused by the presence of ubiquitous surface contaminants, such as carbon and oxygen, than by nickel nanoparticles, since a similar microstructure can be seen in deposition on Si(100) substrates as well.

Pure Silane Growth – Hydrogen dilution effects

We used TEM and Raman Spectroscopy to determine the structure of Si thin films grown at 380°C with graphite wires at 2100°C. We found that the crystallinity did not increase with hydrogen dilution as expected[7]. Instead, an amorphous/protocrystalline structure is observed at dilution ratios of 20 to 30, while at both the 40 and 10 H_2/SiH_4 dilution ratios we observe epitaxial growth with polycrystalline breakdown. This suggests a complex interaction between pressure and dilution, which will be discussed later.

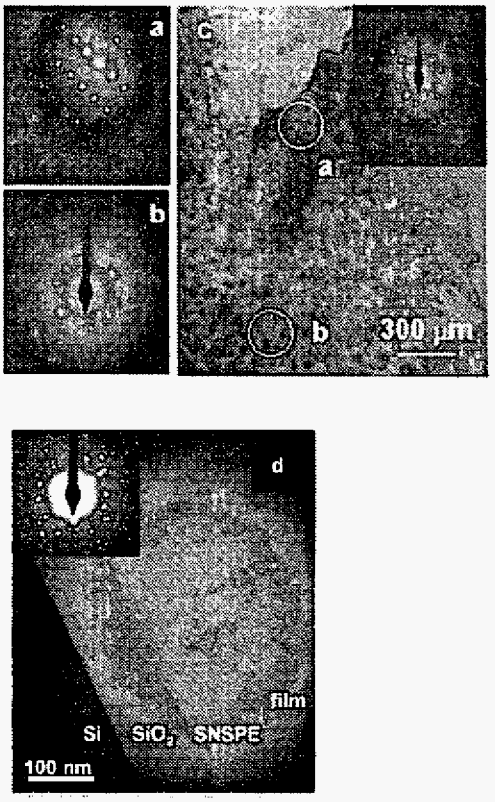

Figure 2: Plan-view TEM of HWCVD epitaxial film (T=300°C) on SNSPE template. (a) Selected area diffraction pattern from underlying SNSPE template. (b) Selected area diffraction pattern from HWCVD film on SNSPE template. (c) Bright-field image indicating selected area diffraction regions. Inset: diffraction from entire area. (d) Bright-field image of HWCVD film (T=300°C) on SNSPE template showing selected area diffraction region. Inset: selected area diffraction pattern showing areas of large-grained polycrystalline growth.

Hydrogen Dilution Ratio	Pressure (mTorr)	Deposition Rate (nm/min)	Raman Crystallinity %	Phase
50:1	50	4	83	Poly
40:1	27	5	84	Epi/poly
30:1	20	3	9	a-Si/Proto
20:1	20	6	10	a-Si/Proto
10:1	20	9	96	Epi/poly

Table 1: Results of HWCVD growth with pure silane at 380 °C substrate temperature and at 2100 °C graphite filament temperature with 3.5cm spacing.

Minority Carrier Lifetimes of HWCVD Films

The minority carrier lifetimes of 1.5–15 μm thick films grown at 300 °C on Si(100) and SNSPE templates were determined through resonant-coupled photoconductive decay (RCPCD) measurements[8]. These films began with epitaxial growth which broke down to microcrystalline growth at thicknesses between 1 – 2 μm. Although the microstructure of these films is mostly microcrystalline, the lifetimes are microseconds long. The lifetimes for films on Si(100) range from 5.7 to 14.8 μs while those for films on SNSPE templates range from 5.9 to 19.3 μs under low level injection conditions, as summarized in Figures 3 and 4. Residual nickel present in the SNSPE templates does not significantly affect the lifetime of films grown on SNSPE templates, making the growth of epitaxial layers by HWCVD on SNSPE templates a viable strategy for the fabrication of thin film photovoltaics.

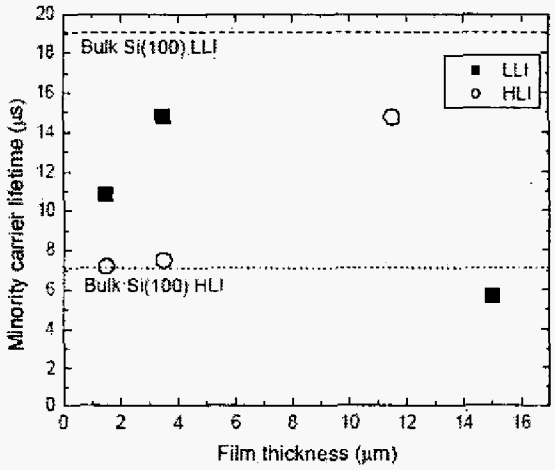

Figure 3: LLI and HLI minority carrier lifetimes of HWCVD films on Si(100) as measured by RCPCD. The dashed and dotted lines represent the LLI and HLI lifetimes, respectively, of the bulk Si(100) substrate.

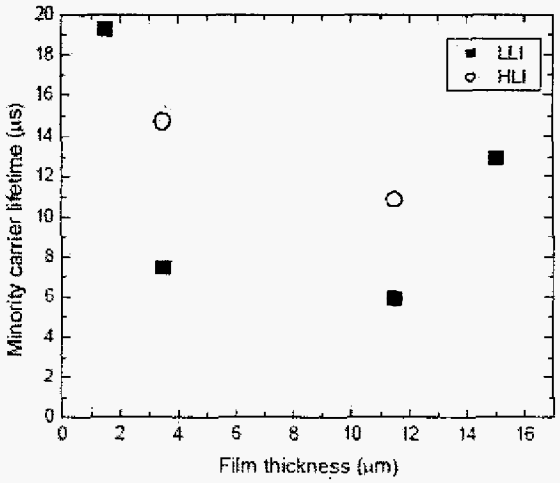

Figure 4: LLI and HLI minority carrier lifetimes on SNSPE templates.

DISCUSSION

Hot Wire CVD – A simple model

The epitaxial growth and growth breakdown trends described above are consistent with a simple model correlating epitaxial growth breakdown with surface oxidation. Starting with an initial hydrogen surface coverage dependent only on the substrate temperature determined from TPD data[9], the model determines the steady-state surface hydrogen coverage by balancing thermal desorption of surface hydrogen with adsorption and abstraction of surface hydrogen by atomic hydrogen produced by the hot wire. Oxygen atom can be incorporated into the film at any empty sites. We used the model to determine the amount of oxygen deposited during the growth of the first monolayer of silicon for a given growth temperature as a function of dilution ratio R ($R=H_2/SiH_4$) at constant pressure, assuming that all silicon atoms incident on the substrate contribute to growth.[5]

Figure 5 shows that the maximum silicon to oxygen ratio decreases with temperature for between 311°C and 520°C at a hydrogen dilution ratio of 50:1. This may explain the decrease in epitaxial thickness with temperature (Fig. 1).

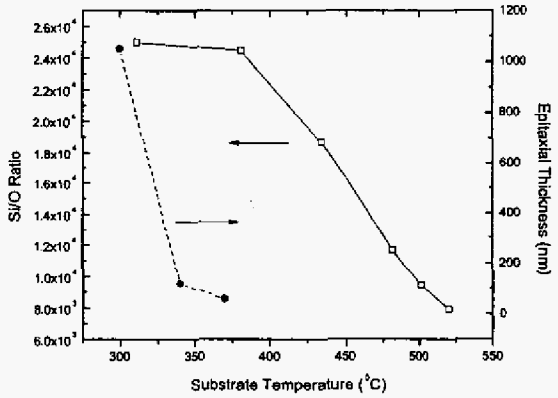

Figure 5: Silicon to oxygen ratio in the first monolayer of growth as a function of substrate temperature for dilute silane growth at 50:1 hydrogen dilution and epitaxial thickness.

The dependence of the epitaxial thickness on the silicon to oxygen ratio is difficult to quantify. However, it is known that, during MBE crystal growth, impurities at the growing interface can lead to surface roughening and subsequent epitaxial breakdown through the formation of voids which may lead to twinning and surface facets[10]. For our dilute silane experiments, a decrease in the maximum silicon to oxygen deposition ratio with temperature, as predicted by the model, may explain the observed decrease in epitaxial thickness with temperature.

Figure 6 may also give some qualitative insight into the amorphous/protocrystalline peak at intermediate dilution for growth with pure silane. In this simulation the deposition pressure is changed along with the dilution ratio

in order to match the deposition conditions in Table 1. The Si/O ratio is highest at the two extremes of the deposition conditions: low dilution ratio, low pressure; and high dilution ratio, high pressure. The high Si/O ratio correlates with a higher degree of crystallinity. A low Si/O ratio leads to the amorphous and ultimately protocrystalline film. Through these experiments and simulations we are working toward determining the optimal deposition parameters for epitaxial growth with polycrystalline breakdown.

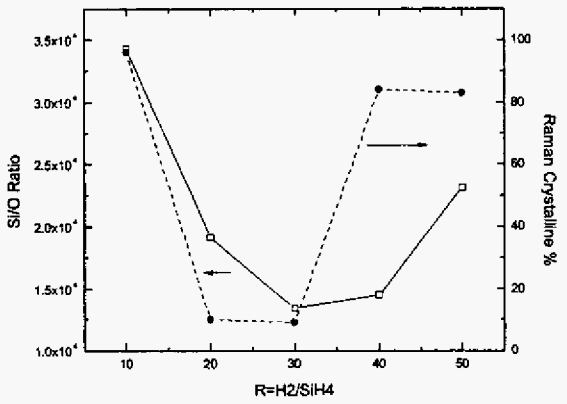

Figure 6: Silicon to oxygen ratio in the first monolayer of growth as a function of R for pure silane growth using the deposition conditions in Table 1 along with the Raman crystalline %.

CONCLUSIONS

We have explored the phase space of HWCVD growth with dilute and pure silane at various substrate temperatures and dilution ratios. The complex interaction between deposition parameters can be qualitatively explained by an oxidation model. Twinned epitaxial growth of Si to thicknesses over 1 μm is observed with polycrystalline breakdown under dilute conditions.

The minority carrier lifetimes of nearly-intrinsic epitaxial/microcrystalline films grown on Si (100) by HWCVD range from 5.7 to 7.5 μs. The lifetimes of films grown under the same conditions on SNSPE templates range from 5.9 to 19.3 μs, making them suitable for incorporation into photovoltaic devices. In particular, residual nickel from the SNSPE templates does not appear to be significantly detrimental to the lifetime of films grown on these templates. If the mobilities in these films are also high, it is possible that HWCVD epitaxy on large-grained SNSPE templates could be a viable strategy for the fabrication of thin-film photovoltaics.

ACKNOWLEDGEMENTS

The authors would like to thank C.M. Garland for her TEM analysis of the films on templates and R.K. Ahrenkiel for the RCPCD measurements. The authors would also like to thank BP Solar, NREL, and Corning Inc. for their financial support.

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